

The Hard and Soft States in Ductile Metals.

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The Micro-structure of Hard-drawn Gold Wires.

In connection with the previous research* attempts were made to break down the crystalline structure of the metal as completely as possible by wire drawing. On etching the surface of wires prepared in this way the structure disclosed appeared to be finely granular, no traces of crystalline grains or of patches of uniform orientation being visible. After the publication of the former paper the wires which had been then used were subjected to a more searching examination. Specimens were ground so as to expose longitudinal sections at various depths and these were etched till the true understructure was disclosed. At low magnifications the structure appeared to consist of parallel strands or fibres which became thinner and either pinched out or drew closer together at the point of fracture. The general character of this structure is shown on fig. 1, which is a diagrammatic sketch of the fractured end of a hard-drawn gold wire.

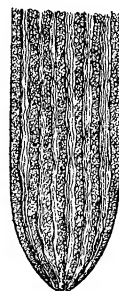
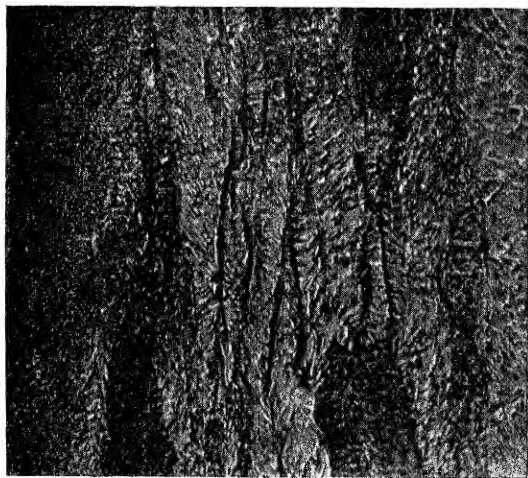


FIG. 1.

For the proper resolution of the intimate structure of these strands or

FIG. 2.—Magnification $\times 700$.FIG. 3.—Magnification $\times 700$.

* 'Roy. Soc. Proc.,' A, vol. 76, p. 462.

fibres, a lens of fairly high N.A. is necessary, and in the photomicrographs, figs. 2 and 3, a 4-mm. objective of 0.95 N.A. was found most suitable.

On fig. 2 the etching has not penetrated very deeply, and portions of the surface are still covered by the remains of the disturbed layer which had been produced by the grinding and polishing; but on the lighter parts of the

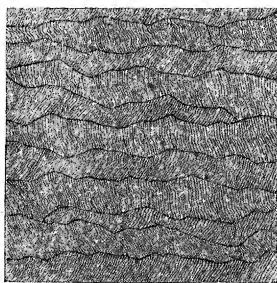


FIG. 4.

photograph the internal structure is plainly disclosed, and it is seen that the strands or fibres are composed of grains which have been drawn out and pinched into long torpedo-like forms. Fig. 4 is a diagrammatic sketch of this type of structure.

Fig. 3 shows the effect of etching away still more of the matrix of amorphous metal, and with it the smaller fragments of crystalline grains. In photographing this specimen, as the irregularity of the surface made it impossible

to get more than a small part in perfect focus at one time, that adjustment of focus was chosen which gave the best general idea of the arrangement of the comparatively large masses which have survived the severe treatment of wire drawing. The material which has been removed from between these ridges is the more soluble, but also the more mechanically stable, amorphous metal which has acted as a rigid matrix to the deformed grains which are enclosed within it. During the successive stages of stretching it seems probable that within any given portion of the wire the rôles of protector and protected may be taken in turn by the substance of adjoining grains. A breakdown of structure occurring in certain grains or lamellæ will result in the momentary production of a relatively large quantity of the mobile phase at the rubbing surfaces, so that for this moment the line of least resistance will be through these grains which will, therefore, take the chief part in the adjustment of strain. But the momentary mobility having given place to the rigidity of the hardened state, this will become the line of greatest resistance, and the stress will now fall on the adjoining grains or lamellæ, which will in their turn break down and flow and in so doing will play their part in the adjustment of strains. Under an augmenting stress, these alternations will naturally continue till the rigidity of the matrix as a whole becomes so great that it will break rather than yield. The present observations show that this stage is reached while there are still comparatively large masses of crystalline substance which have been concreted into rigidity by the flow which has occurred at surfaces within the mass. These masses do not consist of uniformly

oriented lamellæ, but are a conglomerate made up of deformed lamellæ cemented together by flowed metal (fig. 3). These results confirm the conclusions of the earlier research, that the mechanical stability of the amorphous state gives even to the thinnest films an extraordinary power to protect from further destruction the masses of crystalline phase which they enclose.

The persistence of the crystalline phase under the most severe mechanical treatment is well illustrated in the case of gold leaf. In my earlier observations on thin metal films I adopted Faraday's conclusion, that when a gold leaf is floated on a solution of potassium cyanide, the metal is uniformly reduced in thickness by the action of the solvent. Subsequent observations have satisfied me that this is not the case. The cyanide does not proceed by dissolving away the surface uniformly, but it first attacks the amorphous metal, removing it and penetrating right through the substance of the leaf, so that the attenuated film which remains is a skeleton built up of the minute units of the crystalline phase which have survived the severe ordeal of beating. These units are, of course, much too minute to exhibit any crystalline micro-structure, so that but for their difference in solubility they would have escaped detection. A gold leaf may be compared to a light gauzy fabric which has been stiffened by a coating of gum or starch. As the removal of the gum by solution will restore the fabric to its original openness and pliability, so the removal of the flowed amorphous metal by solution leaves the gold leaf with an open spongy texture. A leaf which has been treated in this way absorbs water like a sponge, and in the wet condition appears to have a thickness much greater than that of the original leaf. When spread on a glass plate and dried it becomes less transparent, owing to the replacement of the water by air, and at the same time the appearance of thickness vanishes. The failure of the drastic operation of gold beating to convert the whole of the metal of so thin a film into the amorphous phase suggests that the complete conversion cannot be effected by any purely mechanical process. Observations on the thickness of the surface layer developed by polishing show that the apparently homogeneous layer to which the liquid-like surface is due is not many molecules in thickness, even though the mechanical disturbance penetrates to a much greater depth. As this subject will be fully discussed in another communication, it is not necessary to refer to it further in the present connection.

For the metallurgist and the engineer these observations are of importance, in so far as they show that the hardness which is conferred on ductile metals by any form of cold working is due to the development of a structure in which the distorted remains of the crystalline units are cemented together by a portion

of the metal itself which has momentarily flowed around them, and has then congealed into a harder and more resistant form of the metal. Among alloys, metallurgists are familiar with many cases in which rigidity is conferred by the concreting action of one of the constituents separated during crystallisation, but in the pure metals hardening does not result from the building up of a new crystalline structure, but from the breaking down and flow of the already existing structure. By a single blow with a hammer, a crystal of ductile metal is instantly transformed, so that its mechanical properties are as completely changed as if the metal had been converted into a new compound by alloying. This transformation certainly does not depend on the presence of foreign substances or of mixed constituents, for the property of hardening is not in the least diminished by the most careful purification of the metal. It is quite as marked in the purest specimens as in those which are much less pure.

The observations which follow were made with the object of defining more accurately the temperature range over which crystallisation and the striking changes in physical properties which accompany it take place in metals in the hardened state. The specimens used were obtained from the same sources as those used in the earlier researches. The gold had a purity of 9997, the copper of 9993, and the silver of 10,000.

The Crystallisation Temperature of Hardened Gold.

The crystallisation of various ductile metals has been studied, but the most complete series of observations has been made on gold, partly because it does not oxidise or tarnish on heating, and partly because it is rather less difficult to develop the crystalline structure by etching in gold than in silver or copper.

Specimens from the hard-drawn gold wires prepared in the earlier experiments, and having the micro-structure shown in figs. 2 and 3, were ground and polished and were then heated in an air bath for one hour at temperatures ranging from 195° to 335°. They were afterwards etched in warm *aqua regia* in which a good deal of gold had already been dissolved. The microscopic examination of the etched specimens was made by normally reflected light with lenses of 0.65 and 0.95 N.A. These lenses were preferred to the immersion lens of 1.4 N.A. on account of their greater depth of focus. Depth of focus was specially important, as the etching was conducted so as to bring out the crystalline grains in relief, and not merely as the traces of geometrical figures on a perfectly flat field. This relief was brought more clearly into view by giving to the illuminating beam a slight obliquity, so that there was a considerable play of light and shadow among the different

crystalline facets. In tracing the changes of structure brought about by heat, attention was directed, firstly, to the disappearance of the strained type of structure (figs. 2 and 3) and, secondly, to the appearance of a new crystalline structure (figs. 5 and 6).

Microscopic appearance of the etched specimens :—

- | | | |
|----|----------------------------|---|
| 1. | Heated for 1 hour at 195°. | Distorted grains unchanged (figs. 2 and 3). |
| 2. | „ „ 215°—219°. | Distorted grains still unchanged. |
| 3. | „ „ 225°—230°. | „ „ disappearing. |
| 4. | „ „ 258°—267°. | New crystalline masses but no grains. |
| 5. | „ „ 278°—284°. | Well-formed crystalline grains (fig. 5). |
| 6. | „ „ 320°—330°. | „ „ „ |

Fig. 5 shows the structure of No. 5 at a magnification of 700 diameters. The differently oriented grains and lamellæ can be distinctly traced on the photograph, but were of course much more plainly seen in the microscope, as the natural advantage of the accommodation of the eye, as well as the power of rapidly focussing the microscope from one plane to another, have to be sacrificed when the image is received directly on the photographic film.



FIG. 5.—Magnification $\times 700$.

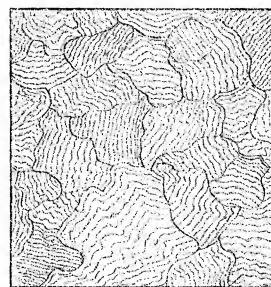


FIG. 6.

A diagrammatic sketch of this structure is, therefore, given on fig. 6 for comparison with the similar sketch of the distorted structure.

This great change of structure has been brought about in the solid metal at a temperature 800° below the liquefying point and by a temperature rise of only 50°.

The disappearance of the distorted structure which set in about 225° was clear and unmistakable, as was also the appearance of the definitely oriented

crystals at 278°. The intermediate changes of structure were more difficult to follow, but the impression gained from frequent re-examination of the specimens was that regular orientation sets in from many centres simultaneously, the oriented units being small but numerous. As the kinetic energy of the molecules rises with the temperature, the larger of these units impress their own orientation on their smaller neighbours, and thus absorb them. This process of growth is only arrested when the smaller units have all been absorbed and the surfaces of the larger crystal grains are in contact with each other. With each rise of temperature a new state of equilibrium among the grains is quickly established, and no re-adjustment of their various spheres of influence takes place thereafter till the kinetic energy of the molecules is again increased by a further rise of temperature. The exact conditions of crystalline growth at higher temperatures have not been studied, but there are definite indications that growth and re-adjustment of equilibrium may continue at temperatures considerably above 300°.

The Effects of Heat at Various Temperatures on the Mechanical Stability of Hard-drawn Wires.

The term "mechanical stability" is used here in preference to the more specific terms "hardness" or "rigidity." It has been shown that wire-drawing can be carried to a point at which a certain condition of mechanical stability is reached, so that the wire will break practically without further extension, if a sufficient stress is applied. The ductile metals show their highest tenacity when they are in this condition, and, owing to the relatively small amount of molecular slipping or displacement which occurs before fracture, it may be accepted that the rigidity and the tenacity break down practically at the same point. This state of stability, therefore, supplies a definite and convenient starting point from which to measure any reduction in stability which may result from heating the hardened metal at various temperatures. For the purpose of the present research it was decided to measure the alterations in stability, not by the "yield-point" as usually understood, but by the stress required to produce a permanent extension of 1 per cent. The standard extension was fixed at this amount only after considerable experience on the behaviour of hard-drawn and annealed wires had been accumulated in this and previous researches. The results obtained by its use show that while considerable irregularity is found in the earliest beginnings of yielding, yet after a 1-per-cent. extension is reached the strain responds fairly promptly and regularly to changes of stress.

The oven in which the hard-drawn wires were heated consisted of a thin

steel tube about 5 mm. in diameter and 1 metre long, through which a current up to 125 ampères could be passed. The current was regulated by a water-cooled resistance, while the temperature of the tube was watched by means of a thermo-electric pyrometer. The uniformity of the temperature along the tube was tested once for all by moving the thermo-couple from end to end and noting the temperature. In this way it was found that, with the exception of a short distance at either end, the temperature was practically uniform throughout. The wires annealed were 500/600 mm. long; they were slipped into a thin glass tube which in turn was slipped into the steel tube so as to occupy its middle portion. I am indebted to Mr. Frederick Soddy for the suggestion of this method, and for fitting up for me the necessary apparatus in which it could be carried out.

As the available supply of silver wire of uniform quality was, in the first instance, all required for the E.M.F. tests, the principal series of stability tests were made with gold and copper, but after the conclusion of the E.M.F. observations a few stability tests were made with silver wire.

The hard-drawn gold wire had a tenacity of 14.6 tons per square inch; this corresponded with an actual load of rather over 13 lbs. on the wire. Under this load the wire stretched less than 0.3 per cent., and then yielded no further. The load of 13 lbs. was then applied to wires which had been heated at 30°, 100°, and 200°, and in no case did the extension exceed 0.3 per cent., the stability, therefore, was still unimpaired. A wire which had been heated at 225° was loaded with 12¾ lbs., and stretched 0.7 per cent. From the behaviour of the next wire after heating at 235°, it was judged that the 225° wire would have stood the full load of 13 lbs. without stretching more than 1 per cent. The 235° wire was gradually loaded with 12 lbs., and only stretched 0.3 per cent., but on increasing the load to 13 lbs. it broke without any general stretching. The measurement of the broken pieces showed an extension of rather less than 1 per cent. While the last two wires fully conformed to the arbitrary standard of stability, their behaviour indicated that a slight impairment of stability had set in. The 250° wire was gradually loaded to 13 lbs., and stretched exactly 1 per cent. The 260° wire showed the first failure to reach the full standard; it was gradually loaded to 12 lbs., and stretched 1 per cent. The 270° wire broke at 11.6 lbs., and the measurement of the pieces showed that it had stretched 1 per cent. The 280° wire, gradually loaded to 11 lbs., stretched rather less than 1 per cent., but when the load was increased to 11½ lbs. it stretched rapidly and broke. The measurement of the pieces showed an extension of 5 per cent., of which 4 per cent. had occurred under the last

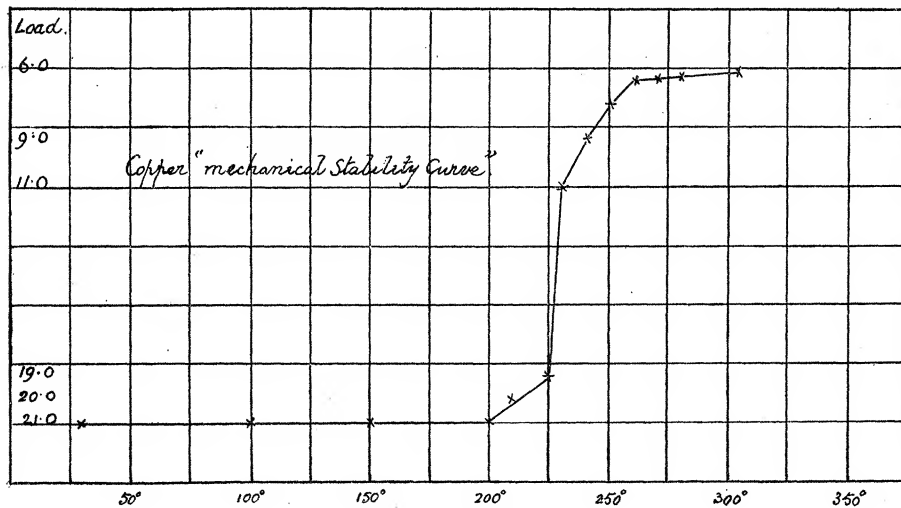
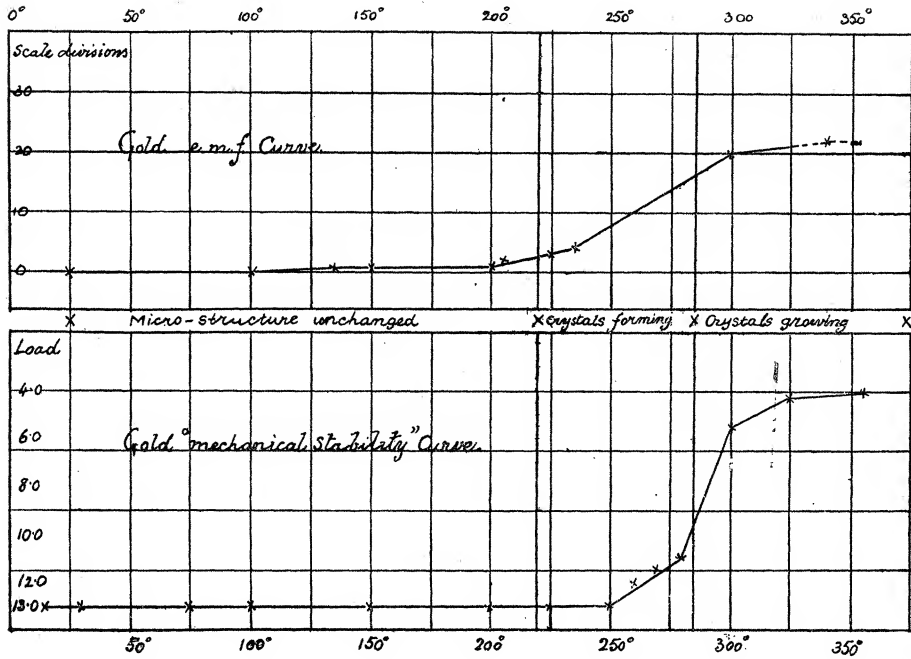
$\frac{1}{2}$ lb. of load. It is to be noted that this serious reduction of stability occurred at 280° , which is the temperature at which well-developed crystalline grains were first visible (fig. 5). The 300° wire stretched 1 per cent. with a load of $5\frac{1}{2}$ lbs., and the 355° wire gave a similar extension at 4 lbs. The latter is equal to a stress of 4.55 tons per square inch; the stability has thus fallen to less than one-third of its original value, the chief part of the reduction having occurred under an increase of 100° in the annealing temperature.

The tests with copper wires showed the unexpected result that hardened copper begins to lose its stability at a lower temperature than gold, and that the loss proceeds much more quickly thereafter. The full load of 21 lbs., which was still carried by the wire at 200° , had to be reduced to 19 lbs. for the 210° wire, though at this point the extension was rather less than 1 per cent. With the 230° wire a load of 11 lbs., or little more than half the original load, produced an extension of 1.1 per cent. A minimum load of 6 lbs. was reached by the 305° wire; thus the stability had fallen to 0.28 of its original value under an increase of less than 100° in the annealing temperature. The stability curves of gold and copper (figs. 8 and 9) are shown in an inverted position for more convenient comparison with the E.M.F. curve (fig. 7).

Mechanical stability in the foregoing observations refers to that property as it exists in the mass of metal as an aggregate. Up to a certain point the stability diminishes as the crystallisation becomes more complete; but even in the wires annealed at the higher temperatures the size of the crystalline grains is small when compared with the whole cross-section of the wire. It is probable, therefore, that the stability of even the softest aggregate is much higher than that of the individual crystals. In gold, the aggregate stability fell to 4.55 tons per square inch, but it may safely be assumed that this does not represent the minimum stability of the individual crystalline units. This has an important bearing on the behaviour of metals under alternating stresses. When the theory of hardening by flow was first put forward by me in 1904,* it was then pointed out that the theory might be applied to the elucidation of the disintegration of metals under alternating stresses. So far as I am aware, this has never been done, and this application will therefore be shortly developed here.

Wherever the effects of alternating stresses on the micro-structure have been carefully observed, as in the researches on iron and steel of Ewing and Humphrey, and of Stanton, it has been found that the cracks which led to the ultimate destruction of the specimens generally passed through ferrite

* 'Phil. Mag.,' August, 1904.



FIGS. 7, 8, 9.

grains or areas. Ferrite grains consist of pure iron in its crystalline or softest state. From the analogy of other ductile metals it may be concluded that the stability of the ferrite grains is much less than that of the aggregates

in which they occur, so that a stress which would be insufficient to produce permanent strain in the aggregate would, if it could gain access to them, be more than sufficient to break down these crystalline units.

It is necessary, therefore, to consider in what way disintegrating stresses can gain access to these elements in the mixed structure. It will be shown in the last section of this paper that while the crystalline phase is more perfectly elastic than the hard phase, yet that the amplitude of the vibrations is greater in the latter state. In a reed vibrator the vibrations of the tongue when it is in the hard state are slower but more ample than when it is in the soft state; the hard tongue is less elastic, but more springy. In an aggregate composed of the two phases which is subjected to rapidly alternating stresses, the hard elements may for this reason be able, with safety to themselves, to transmit stresses which will unduly strain the soft elements.

Consider, now, the part played by the mobile phase through which the crystalline passes into the hardened state. In the opening section, the study of the hardened structure, produced by wire-drawing, showed that this structure owes its hardness and stability to the cementing or concreting effect of the flowed metal, while in an earlier paper it was shown that it is possible to overdraw a wire and thus to reduce its hardness and tenacity. *The latter result may be taken to mean that, during the final drawings, the mobile phase was not produced in sufficient quantity to cement together again the surfaces at which slipping had occurred.* Something of the same nature must occur at the surfaces of slip caused by alternating stresses. When the stress is reversed, slip will occur in the opposite direction, but not on the identical plane on which it occurred before, for the cementing action of the hard phase will prevent this. Suppose the second slip to occur at a thickness of one lamella from the first, a new layer of hard phase will be formed at the other face of the intervening lamella, and a sheet of crystalline phase will thus be sandwiched between two hard sheets. The next reversal of stress may find the sandwiched lamella so strengthened that it can resist further slipping. But suppose that one result of the formation of the sandwich has been to leave the crystalline lamella under a slight tension normal to the surfaces, then with each reversal of stress there will be further slips, and the thickness of the hard sheets will increase at the expense of the crystalline substance. Eventually, if the process continued, and assuming that the tension also continued, the whole of the crystalline material would be used up in thickening the hard sheets, and an incipient crack would develop between them, which, in the absence of further supplies of the mobile phase, every additional slip would rub into greater distinctness.

In fig. 10, these steps are shown diagrammatically.

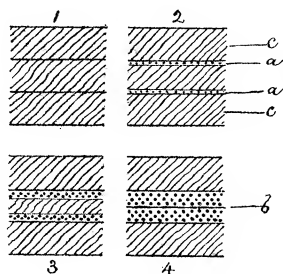


FIG. 10.—1. Unstrained lamellæ in *c* phase. 2. Layers of hard phase *a* formed by slipping. 3. Layers thickened by further slipping. 4. *c* phase all used up and a crack, *b*, developing.

Thermal E.M.F. between Hardened Wires which have been heated at Various Temperatures.

In a former paper* the thermal E.M.F. between silver in its hard and soft states was determined by gradually heating the couple till the maximum deflexion of the galvanometer was reached. The temperature at which this occurred was in the neighbourhood of 250° . It was then realised that this method could only be expected to give satisfactory results if the hard wire of the couple retained its hardness unimpaired till a definite transition temperature was reached. The observations themselves showed that this was not the case. In the newer experiments it was, therefore, arranged that the couples should not be heated above the temperature at which the hard wire would retain its permanent hardness unimpaired. Preliminary experiments showed that by heating to 100° hard wires could be brought into a stable condition while their hardness was only slightly impaired; this was, therefore, selected as the upper temperature to which the couples were to be heated for the development of their thermal E.M.F. The soft wires of the couples were prepared by heating hard wires to various temperatures in the electrical oven already referred to. After heating, it was necessary to handle the soft wires with great care, so as to avoid straining them by bending or twisting. The two wires of the couple were slipped through separate glass tubes, and the junction was made by binding the projecting ends together with very fine silver wire. The junctions with the galvanometer leads were kept at 17° . The couples were heated to 100° by plunging them into a glass tube through which steam was freely blowing at atmospheric temperature; they were cooled by dipping them in water at 17° . The temperature difference for which the E.M.F. was taken

* 'Phil. Mag.,' *loc. cit.*

was thus only 83° , and it was, therefore, necessary to employ a galvanometer of great sensitiveness. The instrument used was of the Kelvin type, and its resistance was 5 ohms. It was adjusted so that each scale-division was equivalent to 0.054 microvolts. This degree of sensitiveness, while amply sufficient for silver, was less satisfactory for gold. With the former a maximum deflexion of 500 scale-divisions was reached, while with the latter the maximum was only 38 divisions. For this reason many more observations were made with silver than with gold, and the E.M.F. curve of the former has been more fully developed and studied.

A number of hard-drawn silver wires were brought into the stable state by hanging them in a glass tube through which steam was blowing freely. Some of these were reserved as standard hard wires, and the others were heated at various temperatures in the electrical oven. In the principal series of observations wires were heated at 130° , 155° , 175° , 200° , 220° , 240° , 260° , 280° , 305° , 325° , and 380° . Each of these wires was tested in a couple with the standard hard wire and in addition the heated wires were tested in pairs among themselves. These latter tests were a useful check on the former. An example will show the extent to which the two sets of observations were in agreement and will at the same time indicate the order of accuracy of the observations as a whole. Let the letters *a*, *b*, *c*, etc., stand for the different couples, then:—

<i>a.</i>	100° — 200°	heated and cooled between 17° and 100°	gave a deflexion of 65 scale-divisions.		
<i>b.</i>	200° — 220°	"	"	"	86
<i>c.</i>	100° — 220°	"	"	"	156
<i>d.</i>	200° — 240°	"	"	"	215
<i>e.</i>	220° — 240°	"	"	"	125
<i>f.</i>	100° — 240°	"	"	"	280

Therefore—

<i>f</i>	measured in one step		= 280 scale-divisions.
<i>f</i>	"	three steps, $a+b+c$	= 276 "
<i>f</i>	"	two steps, $a+d$	= 280 "
<i>f</i>	"	two steps, $c+e$	= 281 "

Observations were made on the effects of heating hardened wires at temperatures below 100° : in these the couples were heated and cooled by plunging them alternately in water at 17° and in melting ice.

With a couple consisting of silver wires in the hardest and softest states respectively, the maximum deflexion obtained for the temperature difference of 83° was 500 scale-divisions, equal to 27 microvolts. This corresponds with an average of 0.09 microvolt per 1° over the whole range. For the different sections of the annealing range the E.M.F. per 1° was as follows:—

From 100° to 200°,	65	scale-divisions	=	0.035	microvolt per 1°.
200° to 220°,	86	"	=	0.232	" "
220° to 240°,	125	"	=	0.337	" "
240° to 260°,	45	"	=	0.121	" "

In the diagram (fig. 10) the deflexions have been plotted exactly as they were observed, and no attempt has been made to smooth the curve. The rapid increase of E.M.F. over the crystallising range is sufficiently obvious. The branch curve which starts at 0° and runs up to 200° is the result of E.M.F. measurements with hard wires which had not been brought into the stable condition by a preliminary heating in steam. Considerable irregularity at the lower part of the curve was found among wires which had been drawn at different times. These were traced to secular changes of the same nature as those observed by Muir in his experiments on glass-hard steel. Taken in connection with the other observations, the lower part of the curve suggests that the changes which occur up to 200° are largely due to the relief of strains of this nature, but that above this point a fundamentally different change sets in.

The gold curve of E.M.F. (fig. 7) confirms generally the conclusions drawn from the other observations. It will be noted that the steepest part of the curve corresponds with the temperature range within which complete crystallisation occurs.

Heating Curves of the Hardened Metals.

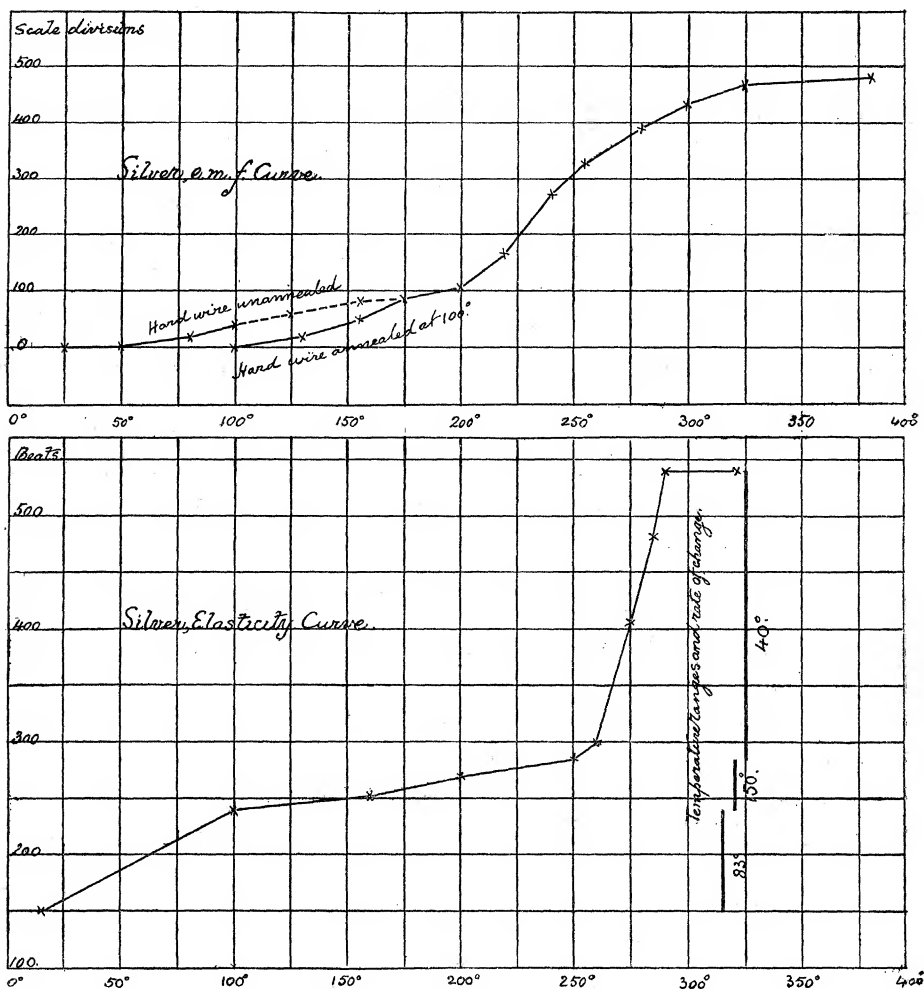
Repeated attempts have been made to obtain heating curves for hardened silver so as to show the evolution of heat over the transition range, but so far the results have not been sufficiently definite to justify their reproduction here. The researches of Guertler* on the transformation of the silicates and borates from the vitreous to the crystalline state show this heat evolution in a very striking way; but these substances, owing no doubt to their high viscosity and low conductivity for heat, lend themselves to this method of investigation in a way which metals with their low viscosity and high conductivity cannot be expected to do.

Acoustical Tests of the Changes in Elasticity due to Annealing at Various Temperatures.

Reed vibrators were prepared in which the vibrating tongues were made of gold, silver, copper, and iron. These reeds could be fitted on a wind chest and sounded in the usual way by compressed air. The pitch of the notes produced was compared with that of the corresponding notes on a

* 'Zeits. Anorg. Chem.,' vol. 40, No. 2, p. 268.

harmonium, the beats being counted with the help of a stop watch. The tongues were annealed by placing the *whole* reed in an air bath, for, had the tongue been removed from the reed for each annealing, there would have been no certainty that its pitch had not been altered in the subsequent readjustment. With the metals experimented on, it was found generally



FIGS. 11, 12.

that the pitch of the hardened tongue was raised from one to two semitones by annealing at the crystallising temperature. The pitch of the vibrators used was in the neighbourhood of $G = 195$ vibrations per second, so that an interval of a semitone was equivalent to about 10 beats per second or 600 per minute. As the pitch could be taken either from the note above or

from that below the vibrator note, it was not necessary to count beats quicker than 300/360 per minute, and this could readily be done with a limit of error not exceeding 2 per cent. A syren was tried instead of the harmonium, but for notes of low pitch the latter was found to be superior.

A complete vibration curve for silver is given on fig. 11. The two stages in the relief of strain which are indicated on the E.M.F. curve are here shown much more distinctly. After rising at the rate of about 1 vibration per 1° up to 100° , the rate of increase falls to 0.3 vibration and remains at this rate till 250° is reached. A fresh increase begins at 250° , which develops at 260° into the final very rapid rise of eight vibrations per minute per 1° over the next 30° . At 290° the maximum elasticity is reached, and further heating to 320° produces no increase in the rate of vibration. This method of measurement lends itself particularly well to the study of secular changes of elasticity in newly strained metal; for example, in one instance the rate of vibration of a freshly beaten silver tongue which was kept at the room temperature of 16° rose 30 beats in three hours.

The amplitude of the vibrations of tongues of gold and silver in the crystalline state is very small, owing to the extreme softness of the metal; indeed, unless a small and very thin tongue is used, the stresses caused by the vibrations are sufficient to cause permanent strain. This was first discovered with a gold vibrator. As the annealing temperature was raised, the rate of vibration increased quite normally up to 250° , but at this point the rate suddenly fell back to what it had been at 100° . The annealed tongue was so soft that at first it could only be sounded by a very gentle stream of air; after continued blowing, a portion of its former spring was restored, but with it a lower degree of elasticity. In the case of the silver vibrator, the first tongue used showed the same effect; it was therefore re-hardened by beating it to one-half of its thickness, after which it showed no signs of reverting to the less elastic condition, even after annealing at 320° .

It is my intention to apply this method in a more extended investigation of the elasticity of metals and alloys at their various critical points.

General Conclusions.

1. A number of new observations have been made on the phenomena which are associated with the hard and soft states in metals. Certain of these have referred particularly to the phenomena as they occur in gold, silver, and copper, being a continuation of a research described in a previous paper on "The Influence of Phase Changes on the Tenacity of the Ductile Metals."* In the course of that research attempts were made to push the

* 'Roy. Soc. Proc.,' A, vol. 76, p. 462.

process of hardening by wire-drawing to its furthest development, the ideal aimed at being the complete conversion of the metal into the hard or amorphous modification. It was then believed that the maximum tenacity would be reached only when the conversion was practically complete.

It has not as yet been found possible to produce a homogeneous specimen of metal entirely in the hard state, for mechanical working, however severe, of even the purest specimens, always produces a mixed structure consisting of the hard and soft phases. The rigidity and tenacity of the hardened metal appear to depend quite as much on the type of structure developed as on the actual proportions in which the two phases are present.

2. As regards the heat treatment of metals in the hardened state, the temperature ranges over which (1) recrystallisation, (2) loss of mechanical stability, (3) development of thermal E.M.F. between wires in the hard and soft states, and (4) the complete restoration of elasticity in hardened metal occur, are all so well marked, and they coincide with each other so closely, that there can be no doubt that they point to the occurrence of a true change of state in the hardened metal when a certain temperature is reached. The nature of this change of state is shown by the microscope to be a development of the crystalline from the non-crystalline condition.

3. In annealing by heat, no important softening of the metal or reduction of mechanical stability occurs till the recrystallisation temperature is reached, but at that point there is a sharp drop in the stability curve, which drop continues as the temperature of annealing is raised over a range of about 50° . Over this range there is a corresponding growth of the crystalline grains. Above this range the curve flattens rapidly, but there is evidence that the crystals may continue to grow further as the temperature is raised. The mechanical stability diminishes as the crystals grow larger, and it is probable that the true stability of the crystalline phase as it occurs in single crystals is considerably lower than that of any aggregate of crystalline grains.

4. The thermo-electric observations, especially those on silver, show that the thermal E.M.F. is an exceedingly delicate indicator of a state of strain in hardened wires. The observed E.M.F. is therefore in part due to strains of a temporary character and in part to a physical change of state of a fundamental nature. By using as the hard wire of the thermo-junctions a wire which had already been annealed at 100° , these temporary strains were partly eliminated, but the curve obtained still indicated that strains of this type persisted till a temperature of 180° to 200° is reached.

5. The secular changes in hardened metal appear to be limited to the gradual relief of strains similar in kind to the contraction strains observed by Muir in the case of glass-hard steel. This relief of strain differs not

only in degree, but also in kind, from the molecular change which occurs when the crystallisation temperature is reached. The first state is unstable even at ordinary temperatures, while the second is stable up to the lower limit of the crystallisation range. In the first state the relief of strain is not accompanied by any change of micro structure, while in the second a very obvious change occurs.

With reference to these two kinds of molecular constraint in hardened metal, it is now suggested that in the first state the molecules themselves are strained, while in the second state they are merely restrained by their mutual cohesion from turning into a uniformly oriented condition.

6. By using an acoustical test for the detection of minute changes of elasticity in the metal tongue of a reed vibrator, elasticity curves have been obtained which show even more clearly than the E.M.F. curves that the relief of strain by heat occurs in two distinct stages and that the rate of change per degree of temperature is much greater in the second than in the first stage.

7. It is believed that the hardening of metals by chilling from a high temperature is in certain cases due to the development of contraction strains. These strains, if of sufficient magnitude, will lead to the displacement of the molecules from their crystalline orientation at the internal surfaces of grains and lamellæ, thus forming a rigid structure of the mixed phases in the same way as mechanically applied stress would do. From this point of view *the hardening produced by hammering and that produced by chilling are both due to the same kind of molecular change of structure.* The present observations explain for the first time why ductile metals like gold and copper are not hardened when they are chilled from a high temperature. In the case of gold, for example, recrystallisation can occur over the whole range from the solidifying point at 1080° down to the minimum crystallising temperature at 220° . It is clear, therefore, that the contraction strains which occur at any point over this range will immediately be relieved by recrystallisation. In cooling below 220° the contraction is probably too small to give rise to strains of sufficient magnitude to deform the crystals and to produce a hardened condition. From this point of view, a substance with a high crystallising temperature and a high coefficient of expansion is more likely to harden by chilling than one in which these constants are lower.

Substances like the silicates and borates, owing no doubt to their high viscosity, have a comparatively high crystallising temperature; it is, therefore, easy to cool them quickly through the crystallisation range, hence they most naturally pass into the vitreous or amorphous state on cooling. It

would be interesting to ascertain to what extent the hardening of the iron alloys by chilling is due to an increase of viscosity brought about by the added substances.

8. In considering the effects of repeated alternations of stress in metals, it is evident that the endurance of the specimen will be determined not only by the mechanical stability of the aggregate as a whole, but also by the stability of its separate units of structure. In the ductile metals the stability of the crystalline phase is greatly inferior to that of the amorphous phase; this inferiority may at first be completely disguised in a mixed structure composed of the two phases, though it may ultimately make itself apparent under repeated alternations of stress. The present observations indicate why the superior plasticity of the crystalline phase, instead of being in all cases a source of strength in the mixed structures produced by hardening, may actually be an element of weakness.



FIG. 2.—Magnification $\times 700$.



FIG. 3.—Magnification $\times 700$.



Fig. 4.

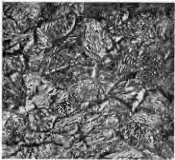


FIG. 5.—Magnification $\times 700$.



FIG. 8.